

SILICATE – CARBONATE SYSTEMS WITH BEARING ON THE ORIGIN AND CRYSTALLIZATION OF CARBONATITES

Peter J. Wyllie.

RESUMO

Abordagens experimentais tentam determinar os meios pelos quais magmas carbonatíticos possam ser derivados de peridotitos portadores de CO_2 , a altas pressões. A associação íntima de kimberlito e carbonatito, em pequena escala, ilustra ligações no processo. Carbonação de peridotito do manto por CO_2 pode causar a geração de líquido carbonatítico quase sólido, a profundidades superiores a 85 quilômetros, dependendo do grau geotérmico.

Para peridotitos cristais com CO_2 e H_2O e composição adequada para a estabilização da flogopita, a composição da fase gasosa é regulada por reações envolvendo carbonato e flogopita. A composição da fase gasosa na fase sólida controla a composição do líquido quase sólido na astenosfera, mas se o carbonato permanece na fase sólida o líquido é provavelmente carbonatítico, com $\text{Ca/Mg} > 1$, e enriquecido em álcalis. Para razões $\text{H}_2\text{O}/\text{CO}_2$ elevadas o líquido na astenosfera superior poderia ser um magma silicático, mas um líquido carbonatítico imiscível rico em álcalis pode separar-se dele.

Evidência experimental a pressões crustais suporta o conceito de magmas alcalinos com nefelina normativa imiscível com magmas carbonatíticos com Ca-Na, ambos coexistindo com fluidos capazes de fenitizar as rochas regionais. Outra evidência demonstra que a cristalização fracionada de magma peridotítico alcalino carbonatado do manto pode produzir seqüências de assembléias minerais muito similares àquelas desenvolvidas em complexos alcalinos com carbonatitos. Minerais acessórios, tais como apatita e sulfetos têm solubilidade limitada em líquidos carbonatíticos sintéticos e portanto eles têm possibilidade de ser co-precipitados com calcita através de amplos intervalos de temperatura em magmas carbonatíticos. A muito baixa viscosidade de líquidos ricos em carbonatos, promove o fracionamento e segregação de minerais em carbonatitos. Texturas minerais em alguns carbonatitos são repetidas experimentalmente. Os dados de equilíbrio de fase são consistentes com a história e a origem magmática dos carbonatitos, embora não haja dúvida que para muitos carbonatitos, a clareza da evidência tenha sido pelo menos parcialmente obscurecida por metassomatismo e recristalização causada por deformação.

ABSTRACT

Experimental approaches attempt to determine the routes by which crustal carbonatite magmas can be derived from CO_2 -bearing peridotite at high pressures. The intimate association of kimberlite and carbonatite on a small scale illustrates links in the processes. Carbonation of peridotite by CO_2 can cause the generation of near-solidus carbonatitic liquid from mantle peridotite at depths greater than about 85 km, the depth depending on the geotherm.

For lithosphere peridotite with CO_2 and H_2O and composition suitable for the stabilization of phlogopite, the vapor phase composition is buffered by reactions involving carbonate and phlogopite. The vapor-phase composition at the solidus controls the near-solidus liquid composition in the asthenosphere, but if carbonate persists to the solidus, the liquid is probably carbonatitic, with $\text{Ca/Mg} > 1$, and enriched in alkalis. For high $\text{H}_2\text{O}/\text{CO}_2$ ratios the upper asthenosphere liquid could be a silicate magma, but an immiscible alkali-rich carbonatitic liquid may separate from it.

Experimental evidence at crustal pressures supports the concept of nepheline-normative alkaline magmas immiscible with Ca-Na carbonatite magmas, both coexisting with fluids capable of fenitizing the country rocks. Other evidence demonstrates that fractional crystallization of a carbonated alkaline peridotite parent magma from the mantle can produce sequences of mineral assemblages very similar to those developed in alkaline complexes with carbonatites. Accessory minerals such as apatite and sulfide have limited solubility in synthetic carbonatite liquids, and therefore, they are likely to be co-precipitated with calcite through wide temperature intervals in carbonatite magmas. The very low viscosity of carbonate-rich liquids promotes fractionation and the segregation of minerals in carbonatites. Mineral textures in some carbonatites are duplicated in experimental runs quenched from fields for the coexistence of crystals + liquid. The phase equilibrium data are consistent with magmatic origin and history for carbonatites, although there is no doubt that for many carbonatites the clarity of the evidence has been at least partly obscured by metasomatism and recrystallization caused by deformation.

INTRODUCTION

The problem of the origin and crystallization of carbonatites covers a wide range of pressures, temperatures, and compositions. The parent magma from which carbonatites and associated alkaline rocks are derived must originate in the mantle, with some variety of peridotite as its source. The end product composed largely of carbonates, with its concentration of rare and desirable elements, represents an extreme of differentiation from the source peridotite. Carbon dioxide must be present in the source material, unless one is prepared to extract it from the crust, and I am not prepared to accept this. Therefore, we seek experimentally to determine the routes by which carbonatite magmas can be derived from CO_2 -bearing peridotite at high pressures. The only likely processes are the generation of primary carbonatite melts, liquid immiscibility between silicate and carbonate melts, or extreme fractional crystallization of a parent magma under special circumstances.

I believe that kimberlites provide us with important links in the processes between mantle peridotite and crustal

carbonatite. Many petrologists studying the continental associations of alkaline rocks with carbonatite intrusions have appealed to a parent magma described as primary, carbonated alkali ultrabasic magma (King, 1965, for example). Wimmenauer (1966) suggested olivine nephelinite or melilitic ankaratrite magmas as possible sources of the carbonatites of the Kaiserstuhl. These magmas have obvious chemical affinities with kimberlites. I was fortunate enough to attend the First International Kimberlite Conference in South Africa in 1973 (Ahrens et al, 1975), where participants were treated to excellent guided tours deep within many kimberlite pipes. I was surprised to discover how much carbonate was associated with the kimberlites, and delighted to learn that most of the geologists working within the mines were reasonably satisfied that much of this was primary. Perhaps this is already clear from the published literature, but I was not previously aware of it, although I had suspected it from Watson's (1955) petrography, and from our experimental studies (Franz and Wyllie, 1967). Daly's (1925) claim that bodies of carbonate-rich rocks in the Premier mine were of magmatic origin did not receive the attention it appears to have deserved.

The intimate association of kimberlite and carbonatite on a small scale was magnificently displayed in the report of Dawson and Hawthorne (1973) on the layered sill at Benfontein, South Africa. The composite intrusion developed cumulus layers enriched in olivine and perovskite, grading upwards into carbonate-rich layers. The former presence of carbonatite magma in these layers is indicated by the presence of dendritic (quenched) calcite, and the formation of diapirs of carbonate rooted in the carbonate layers and rising through the overlying layers. Figure 1 illustrates some features of the sill, but I refer readers to the original paper by Dawson and Hawthorne (1973) for very detailed illustrations.

Figure 2 shows another example of intimately associated kimberlite and carbonatite that has superficial similarities with the Benfontein material. The delegates of the First International Kimberlite Conference were directed to a vertical dike, 40 cm wide, exposed at the 500 m level in the De Beers Mine, Kimberley. Irregular pods of carbonate (with serpentine) occur in two symmetrical layers parallel to, and close to the margins of the dike. The pods have diapiric form, but they are elongated normal to the dike wall, in a horizontal attitude rather than the vertical attitude of the diapirs in the Benfontein sill. The textures are clearly influenced by chilling along the thermal gradient normal to the dike wall, but the diapirs do exhibit a slight vertical component in their direction.

Kimberlites may be derived from sources hundreds of kilometers within the earth, and Figures 1 and 2 indicate that their crystallization can produce carbonatites if conditions are suitable. The inference is clear that the CO_2 originated from great depths along with the kimberlite magma. High-pressure processes for the generation of kimberlite from CO_2 -bearing mantle peridotite should therefore be related to low-pressure crystallization processes and the genera-

tion of carbonatite magmas. Similar processes are likely to be involved in the petrogenesis of alkali ring complexes with carbonatites.

This is the rationale for studying silicate-carbonate- CO_2 - H_2O melting relationships through the pressure range from asthenosphere to surface.

THE EXPERIMENTAL PROGRAM

There are many different experimental approaches to specific petrogenetic problems. These range from phase equilibrium studies of synthetic systems, or of selected mineral assemblages from a system, to studies of whole rock systems, either assumed source rock or derivative magma, or of any particular rock of interest, or of a whole series of related rocks. For carbonatites, these approaches can be introduced in the historical sequence of the development of my own research program.

O.F. Tuttle was responsible for the initiation of my long-duration experimental program related to the origin and crystallization of carbonatites. One day in 1958, when I was his research assistant, he asked me to see if I could determine the effect of water under pressure on the melting temperature of calcite. The dramatic effect of water on the melting temperatures of feldspars and granite had been established, but exploratory runs in carbonate-water systems had produced no obvious melting. We identified the quench textures in former liquids, and proceeded to determine the phase relationships in the system $\text{CaO-CO}_2\text{-H}_2\text{O}$ at crustal pressures (Wyllie and Tuttle, 1959a, 1960). This confirmed that there were melts of simple composition that could precipitate calcite at temperatures down to about 650°C , in contrast to the 1300°C required for liquids of composition CaCO_3 . There remained no reason to doubt that carbonatite magmas of more complex composition could exist at moderate temperatures when the field evidence was consistent with such an interpretation.

The initial experiments in the system $\text{CaO-CO}_2\text{-H}_2\text{O}$ were followed by a series of studies by my student associates involving systems of increasing complexity. Many of the results at crustal pressures were reviewed at the 1964 International Geological Congress (Wyllie, 1966a; Wyllie and Biggar, 1966), in the volume on "Carbonatites" edited by Tuttle and Gittins (Wyllie, 1966b), and in the volume on "The Alkaline Rocks" edited by Sørensen (Wyllie, 1974). These experiments were related to crustal processes and the association of carbonatites with alkaline rocks.

A second stage in the program was started when my former research associate A.L. Boettcher extended the low-temperature melting reactions in the systems $\text{CaO-CO}_2\text{-H}_2\text{O}$ and $\text{CaO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ from crustal pressures to mantle pressures of 40 kb (Wyllie and Boettcher, 1969; Boettcher and Wyllie, 1969). This brought us to the question of the origin of the parent magmas from which the carbonatites and alkaline rocks were derived, but in order to get to grips with this problem we had to work with reactions occurring at higher temperatures, appropriate for these mantle depths.



Figure 1. Polished rock slab from the Benfontein Sill, Kimberley. The multiple intrusion displays layers of kimberlite overlain by carbonatite. Diapirs of carbonate rooted in the carbonatite layers rise through the overlying mafic layers. The sill was described and illustrated in detail by Dawson and Hawthorne (1973).

A third stage involved the study of mantle-derived amphibole-bearing peridotites and other low-silica rocks, with low water contents controlled in the experimental charges by the presence of hydrous minerals (Millhollen and Wyllie, 1974; Millhollen et al, 1974; Merrill and Wyllie, 1975). We had intended originally to extend these experiments by addition of phlogopite and CO_2 , hoping to link them to the crustal pressure experiments involving higher concentrations of CO_2 and H_2O , but we encountered experimental problems that disenchanted us with this approach (Merrill and Wyllie, 1973; Nehru and Wyllie, 1975). Fortunately, Mysen and Boettcher (1975a, 1975b) were more successful, and they completed studies of peridotite- CO_2 - H_2O with oxygen fugacity controlled as well, relieving us of the responsibility to grapple further with the problems.

The fourth stage involves study of the melting relationships in silicate-carbonate systems at mantle pressures, with CO_2 and CO_2 - H_2O mixtures, with the aim of discovering the principles that control the reactions occurring in natural peridotite-carbonatite- CO_2 - H_2O systems. Experiments have ranged from the simple carbonate systems, CaO - MgO - CO_2 (Irving and Wyllie, 1973; Huang and Wyllie, 1976), to the system CaO - MgO - Al_2O_3 - SiO_2 - CO_2 (Maaløe and Wyllie, 1975; Wyllie and Huang, 1976a), and into CO_2 - H_2O bearing systems involving carbonates and phlogopite. The experiments of Eggler and his associates at the Geophysical Laboratory on silicate- CO_2 phase relationships and solubility studies (Eggler, 1974; Mysen et al, 1976) have recently overlapped into the region of our silicate-carbonate studies (Eggler, 1976). These will doubtless merge satisfactorily with our results in due course, although at present there are some differences in data and interpretations. Brey and Green (1975, 1976a) have also reported experiments on the solubility of CO_2 in olivine melilitite and the role of CO_2 in the upper mantle, which produced a challenge from the Geophysical Laboratory (Eggler and Mysen, 1976; Brey and Green, 1976b).

In this paper we will start with the most recent studies relevant to the mantle sources, and follow the carbonate melting reactions to lower pressures from mantle into crust, with some consideration of crystallization sequences in the differentiated products.

MANTLE PERIDOTITE AND CARBON DIOXIDE

Until recently, available data indicated that the solubility of CO_2 in normal silicate magmas at crustal pressures was very small (Wyllie and Tuttle, 1959b). Recent experiments by Eggler and his associates at the Geophysical Laboratory on CO_2 solubilities in silicate liquids show that solubilities increase to 5-8 weight per cent in the pressure range 10-30kb, for individual minerals such as diopside, and for magmas such as olivine melilitite nephelinite (Eggler, 1974; Mysen et al, 1976).

Huang and Wyllie (1974) determined the phase fields intersected by the joins MgSiO_3 - MgCO_3 and CaSiO_3 - CaCO_3 at 30 kb, and found that there were significant differences between the Mg- and the Ca-system. The results indicated that the CO_2 solubility in the Mg-silicates was low, as reported by Mysen et al (1976), but that there was a binary eutectic liquid containing almost 45% carbonate in the Ca-system; this is equivalent to dissolved CO_2 of at least 20%. The reason for the difference is that wollastonite and calcite coexist at this pressure, whereas enstatite and magnesite react to produce forsterite and CO_2 . The latter reaction has been determined to 40 kb by Newton and Sharp (1975).

Wyllie and Huang (1975, 1976a, 1976b) combined available experimental data in the system CaO - MgO - SiO_2 - CO_2 with phase equilibrium analysis, and produced partly schematic phase diagrams. According to these diagrams, at pressures greater than 25-30 kb, the first liquid produced from the model mantle assemblage olivine plus two pyroxenes ($\text{Fo} + \text{Opx} + \text{Cpx}$) with CO_2 (present as calcic dolomite) was essentially fused carbonate with 10-15% of dissolved

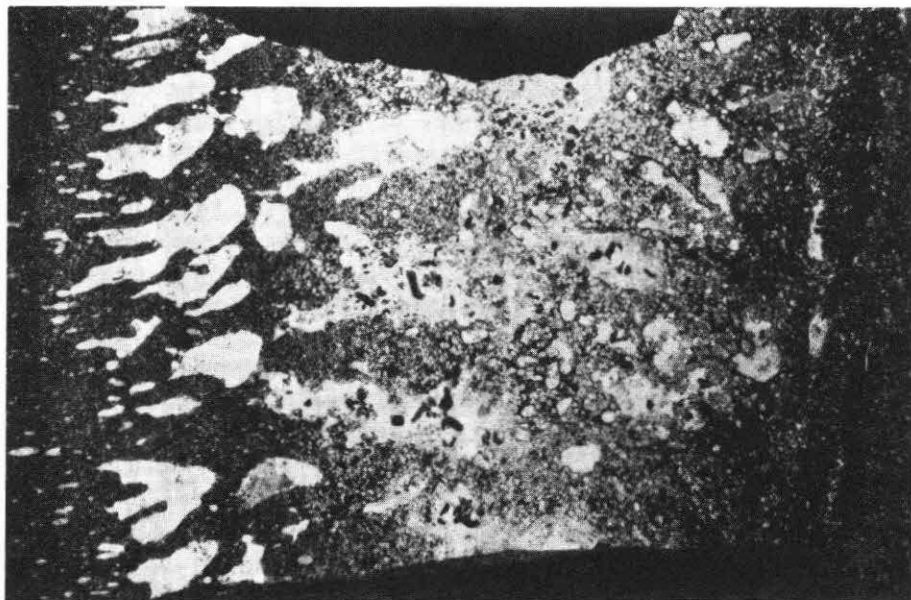


Figure 2. Kimberlite dike with carbonate-serpentine pods arranged in horizontal attitude, perpendicular to the dike margins. The 40 cm-wide dike, exposed at the 500 m level in the De Beers Kimberlite Mine, has these carbonate-rich pods in layers on both sides of the dike. The formation and growth of these features is intimately related to the crystallization of the kimberlite inwards from the dike walls, indicating that carbonate components constitute an integral part of the original kimberlite magma. Compare with the carbonate diapirs in Figure 1.

silicates. This corresponds to a CO_2 solubility approaching 40%. These conclusions were disputed by Eggler et al (1976) and Eggler (1976), but we stick by them (Wyllie and Huang, 1976c), as illustrated in Figure 3.

The explanation for the extraordinarily high CO_2 solubility in the liquid coexisting with the silicate assemblage $\text{Fo} + \text{Opx} + \text{Cpx}$ is given by the reaction illustrated in Figure 4, and its intersection with the silicate- CO_2 solidus at an invariant point, as illustrated in Figure 4. There is a whole series of decarbonation reactions in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$, with starting assemblages involving calcite, dolomite, magnesite and quartz reacting to produce free carbon dioxide and silicate minerals enstatite, forsterite, diopside and wollastonite, among others. Bowen (1940) compared the theoretical sequence of mineral assemblages produced by temperature increase at crustal pressures with the sequence of reactions deduced from the progressive metamorphism of siliceous dolomites. This formed the basis of his petrogenetic grid. The sequence of reactions and subsequent theoretical and experimental work were reviewed by Turner (1968, p 131-151).

Extension of these decarbonation reactions to mantle pressures produces a family of curves involving mantle silicates, CO_2 , and carbonates (Wyllie and Huang, 1975, 1976a). One of these, reaction (6) illustrated in Figure 4, involves all three major mantle minerals, $\text{Fo} + \text{Opx} + \text{Cpx}$, together with a calcic dolomite (Cd.). At constant pressure, the 5 phase assemblage is invariant, and the compositions of the reacting phases are given by the 5-phase tie-figure illustrated in Figure 4 (with tie-lines to CO_2 omitted for clarity).

There are five 4-phase assemblages associated with the reaction, only two of which include all three mantle silicate minerals. The discussion is limited to a model mantle assemblage dominated by Fo. In terms of decarbonation, we see that the assemblage $\text{Fo} + \text{Opx} + \text{Cpx} + \text{Cd}$ dissociates to produce $\text{Fo} + \text{Opx} + \text{Cpx} + \text{CO}_2$. If we consider the reverse

reaction, carbonation, we see that the assemblage $\text{Fo} + \text{Opx} + \text{Cpx} + \text{CO}_2$ with increasing pressure reacts to produce either the vapor-absent assemblage $\text{Fo} + \text{Opx} + \text{Cpx} + \text{Cd}$, or, if there is sufficient CO_2 present, the clinopyroxene becomes completely carbonated to yield the assemblage $\text{Fo} + \text{Opx} + \text{Cd} + \text{CO}_2$. The latter condition is unlikely to be achieved in the mantle where CO_2 concentrations are surely small.

The subsolidus carbonation reaction (6), terminating at the invariant point O_6 where liquid appears, is plotted in Figure 5 according to the data reported by Wyllie and Huang (1975) rather than being slightly displaced for clarity of representation in complex diagrams as in Wyllie and Huang (1967a). The cause of the difference between our curve and that of Eggler (1976) is probably the recurrent problem of friction correction in piston-cylinder apparatus. The use of glass furnace assemblies to reduce migration of water into the sample (Irving and Wyllie, 1975) requires a friction correction different from that required with talc assemblies (Huang and Wyllie, 1975). Eggler (1976) also used the results of Newton and Sharp (1975) for the forsterite carbonation reaction, but found it necessary to correct them by "1.5 kbar to be compatible with runs in figure 2". We checked our calibration (with piston-out method) by reversals of the reaction determined by Newton and Sharp (1975) in different apparatus (with piston-in method), and our results agreed precisely. Therefore, we expect Eggler's results to be higher than ours by about 1.5 kb.

The solidus curve in Figure 5 is divided into two portions, the low-pressure curve below the invariant point, where CO_2 exists as vapor and the CO_2 solubility in the liquid remains low, and the high-pressure curve above the invariant point, where the CO_2 is combined with the peridotite to produce calcic dolomite (Cd in Figure 4). Eggler's (1976) has recently revised his earlier results (Eggler, 1974) on the low-pressure solidus curve, and the pressure maximum shown

by Wyllie and Huang (1975) and reproduced in Figure 5 is no longer required. Eggler's (1976) estimate of dP/dT for the silicate-carbonate solidus rising from I_1 appears to be too low in comparison with the slopes of other silicate, carbonate, and silicate-carbonate melting curves.

Using the geotherms shown in Figure 5, Newton and Sharp (1975) and Wyllie and Huang (1975, 1976a) concluded that free CO_2 does not exist in the mantle under conditions of normal temperature distribution, because, the CO_2 is stored in carbonate (see also Koster van Groos, 1975). Eggler (1976) concluded that free CO_2 would exist in suboceanic mantle. Figure 5 shows that the conclusion is very sensitive to the friction correction applied to the piston-cylinder apparatus; this can change the curve through 2 or more kilobars. It is also sensitive to the geotherm adopted. The Ringwood (1966) geotherms in Figure 5 are located at significantly higher temperatures than those of Clark and Ringwood (1964), for example. It is agreed, however, that CO_2 in subcontinental mantle could not exist as free vapor, but only as carbonate, in mixed CO_2 - H_2O vapors, or in interstitial melt.

The composition of the liquid produced by melting of the silicate-carbonate assemblage along the high-pressure vapor-absent solidus is carbonatitic according to Wyllie and Huang (1975, 1976a), and kimberlitic according to Eggler (1976). In an earlier abstract entitled "Carbonatite generation by reaction relation in the system CaO - MgO - SiO_2 - CO_2 at 30 kbar pressure", Eggler (1975a) stated that "A magnesite-rich carbonatite melt can form at temperatures subsolidus to the silicate phase assemblage". We believe that his first interpretation was more nearly correct in terms of CO_2 content, but incorrect in terms of Ca/Mg ratio. The near-solidus liquid is enriched in dolomite rather than magnesite.

The fundamental difference between the two studies is in the location of the field boundary between the fields for primary silicates and carbonates on the CO_2 -saturated liquidus surface, as illustrated in Figure 3. Wyllie and Huang (1975) have used mixtures on the pyroxene-carbonate join, shown by dashed lines in Figure 3A. Eggler (1976) used mixtures on the joins Di - Fo and La - Fo with excess vapor, which intersect the pyroxene-carbonate join along the dashed lines in Figure 3B. As Eggler (1976) pointed out, "both sets of results involve a certain amount of extrapolation and inference." We made specific efforts to bracket the silicate-carbonate field boundary, and feel confident in the position shown in Figure 3A. Figure 3B shows that Eggler's (1976) location (projected) required extrapolation.

Resolution of the differences shown in Figure 3 is not an academic, phase equilibrium problem. According to Eggler (1976), the liquids in the low-velocity zone would be "broadly kimberlitic", with compositions near B in Figure 3B. I conclude that liquids at the top of the low-velocity zone without H_2O would be carbonatitic, with compositions near E in Figure 5A. These liquids have Ca/Mg ratios greater than 1. With increasing depth, these would grade into kimberlitic liquids nearer B in composition, but undersaturated with CO_2 (Wyllie and Huang, 1976a, 1976b).

MANTLE PERIDOTITE WITH CARBON DIOXIDE AND WATER

Figures 3 and 5 provide one limit for models of mantle processes. The real mantle contains some H_2O and many other components. I have recently prepared a series of partly schematic phase diagrams for the system peridotite H_2O - CO_2 to illustrate the effect of H_2O , and to bring melting temperatures down from the high levels in the synthetic system of Figure 4 to levels more realistic for upper mantle processes. Details of the construction and sources are given elsewhere (Wyllie, 1976). I assume for graphical convenience that carbonation reaction (6) of Figure 4 remains univariant instead of becoming divariant through solution of FeO and Al_2O_3 .

Figure 6A shows an estimate of the peridotite H_2O - CO_2 solidus, contoured in terms of vapors of fixed composition (see Mysen and Boettcher, 1975a). The univariant decarbonation reaction becomes a divariant surface extending to lower temperatures in the presence of mixed CO_2 - H_2O vapors (see Kerrick, 1974, for review), and the surface is mapped by the contours for vapor phase composition.

These two surfaces intersect along the early line extending from I_6 . The P-X projection of the solidus surface in Figure 6B shows more clearly how vapor phase composition changes along the curve of intersection. It also shows intersection curves for two other carbonation reactions, which need not concern us here, and estimates of the isotherms on the surface. In order to examine the involvement of carbonates with melting processes, I assume in these diagrams that the peridotite composition is not suitable for the stabilization of hydrous minerals phlogopite and amphibole.

The heavy univariant line extending from I_6 shows the conditions for the beginning of melting of the carbonated assemblage $Fo+Opx+Cpx+Cd$ in the presence of CO_2 - H_2O vapor. For each vapor phase composition, the pressure-temperature of melting is defined. There is little change in P-T for vapors ranging from pure CO_2 to about 50% H_2O , but with further increase of H_2O/CO_2 in the vapor, the reaction extends to much higher pressures with little change in temperature.

Consider mantle peridotite with excess vapor of fixed composition. Figure 7A shows the solidus and position of reaction (6) for a vapor with 50% CO_2 , reproduced from the contours of Figure 6A. Note the univariant line for other vapors connected to I_6 . The ocean geotherm of Clark and Ringwood (1964) intersects both decarbonation reaction and solidus for this vapor phase composition. Note that the shield geotherm (Figure 5) would not intersect the field for peridotite + vapor at all.

Figure 7B is a geotherm section through the phase diagram for peridotite - CO_2 - H_2O . The vertical axes show the variation in depth (pressure) and temperature along the geotherm, and the two curved lines show the intersection of this P-T trajectory with the two divariant surfaces shown in Figure 6A. Intersections with other carbonation reactions (Figure 6B) have been omitted. The line *abc* in Figure 7B corresponds to movement of material up or down the geotherm along *abc* in Figure 7A, with fixed vapor phase composition.

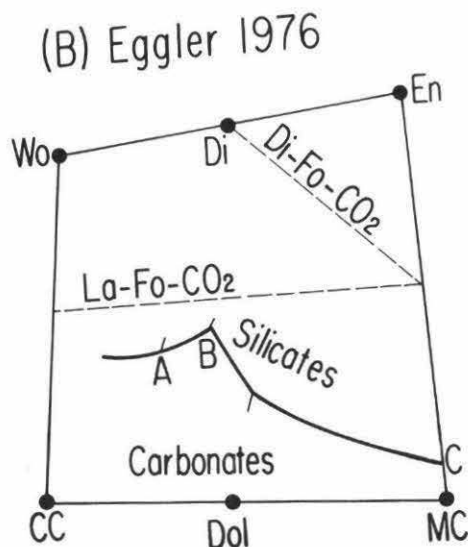
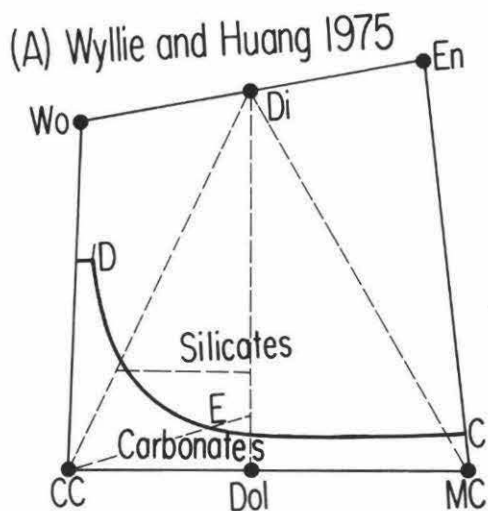


Figure 3. The silicate-carbonate liquids field boundary on the CO_2 -saturated liquidus surface in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$ at high pressures (weight percent), projected onto the pyroxene-carbonate join (compare Figure 4). Dashed lines show composition joins studied by A. Wyllie and Huang (1975), and B. Eggler (1976).

At the invariant point where reaction (6) is joined a liquid

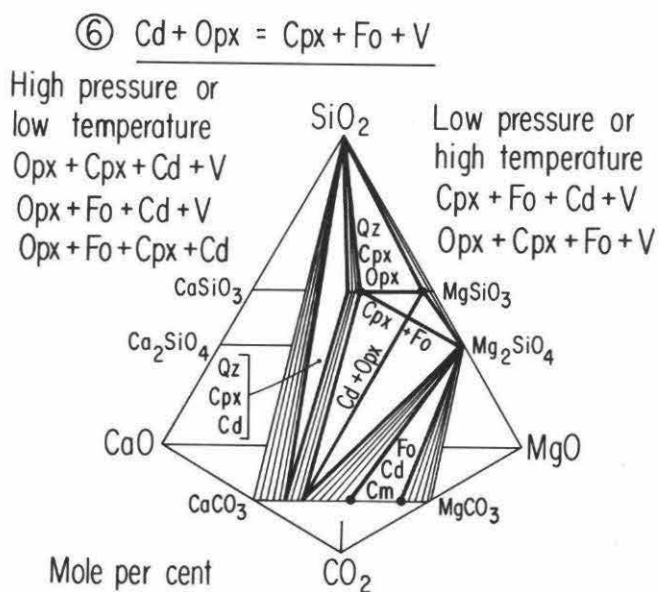


Figure 4. Carbonation of mantle peridotite illustrated by reaction in the system CaO-MgO-SiO_2 . All phase fields shown are connected to CO_2 , but these tie-lines have been omitted for clarity (Wyllie and Huang, 1975). The 5-phase reaction involves five 4-phase assemblages, with the mantle minerals represented by forsterite (Fo), enstatite (Opx), and diopside (Cpx) solid solutions. CO_2 is involved either as vapor (V), or as carbonate (Cd, calcic dolomite). Abbreviations for other phases: Qz - quartz and SiO_2 polymorphs; Cm - magnesite solid solution. The univariant curve for the reaction is shown in Figure 5.

(Q_6 in Figure 5), the liquidus field for orthopyroxene just reaches the silicate-carbonate field boundary (see Wyllie and Huang, 1976 a, for details) near point E according to Wyllie and Huang (1975), and near A-B according to Eggler (1976). Liquid E is carbonatitic, with about 40% dissolved CO_2 , whereas liquid A-B is kimberlitic with 20% CO_2 . We have strong evidence to support the carbonatitic liquid.

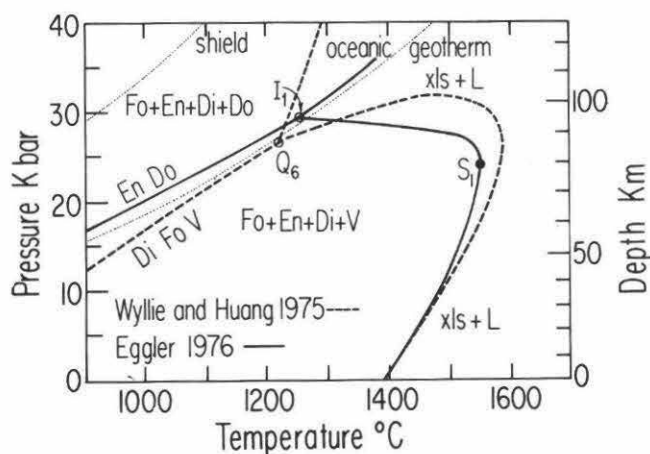


Figure 5. Comparison of two published versions of reactions of model mantle peridotite ($\text{Fo} + \text{En} + \text{Di}$, or $\text{Fo} + \text{Opx} + \text{Cpx}$ as in Figure 4) in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$. There are three univariant curves meeting at an invariant point. The subsolidus carbonation reaction illustrated in Figure 4 terminates where liquid appears. The solidus is divided into two portions, the low-pressure curve below the invariant point. The pressure maximum on the solidus for $\text{Fo} + \text{En} + \text{Di} + \text{V}$ shown by Wyllie and Huang (1975, 1976a) was required because of the constraints imposed by a point for the assemblage $\text{Fo} + \text{Opx} + \text{Cpx} + \text{L} + \text{CO}_2$ reported by Eggler (1974) at 30 kb and 1565°C . Eggler (1976) does not use this point in recent versions of his silicate- CO_2 work (Eggler, 1976), and if the point is not valid then no pressure maximum is required. The geotherms are from Ringwood (1966), displaced to somewhat higher temperatures than those of Clark and Ringwood (1964).

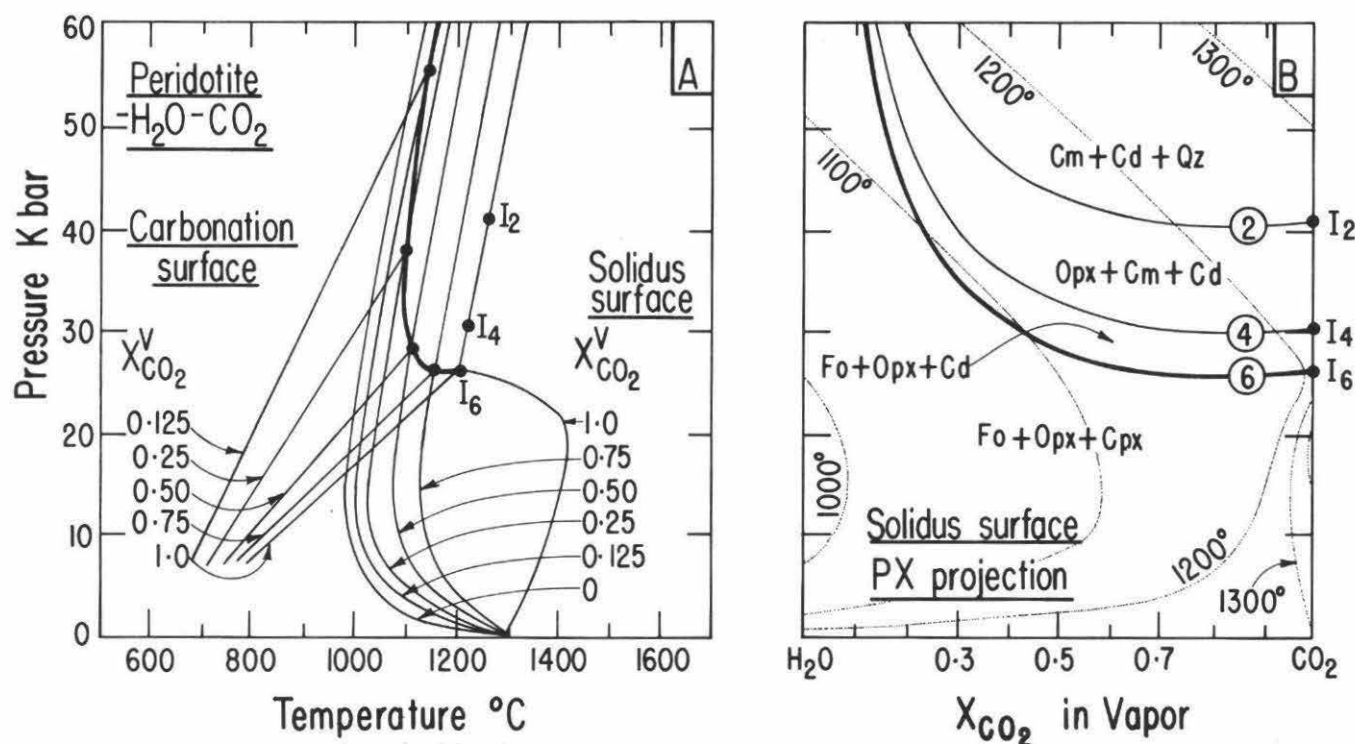


Figure 6. Intersection of divariant carbonation reactions with the divariant solidus surface for peridotite-H₂O-CO₂, excess vapor, schematic, neglecting hydrous minerals. See Wyllie (1976) for details of construction and sources.

A. The solidus surface and the carbonation surface for reaction (6) of Figures 4 and 5 are contoured by lines of constant vapor phase composition. The contours on each surface intersect the corresponding contours on the other surface in

Consider peridotite with vapor just below the solidus temperature, near c in Figure 7. If this moves slowly upwards through the mantle, with thermal equilibrium being maintained, it will react at point b to produce Fo + Opx + Cd. Complete carbonation in this way requires addition of CO₂ to the reacting vapor phase, and more CO₂ than we might expect in the upper mantle. This open system treatment is therefore unrealistic. The vapor phase composition is probably buffered by the mineralogy, under most conditions.

Figure 8A shows the same geotherm section as Figure 7B, and points abc correspond to points on the geotherm in Figure 7A. Assume now that the peridotite just below the solidus near c in Figures 7 and 8A contains only 0.2% vapor of defined composition. Figure 8A shows that if this is cooled under the same conditions by slow upward movement, carbonation begins as before at point b, but this forces the vapor phase to change composition along the reaction surface ba. Carbonation is not completed, and the assemblage Fo + Opx + Cpx + Cd, plus vapor becoming progressively enriched in H₂O, persists through a temperature interval.

Consider partially carbonated mantle peridotite containing 0.1% each of H₂O and CO₂, situated at point a on

a series of points, and the curve through these points is the projected line of intersection of the two surfaces.

B. P-X projection of the solidus surface, showing lines of intersection with divariant carbonation reactions (6), (4), and (2) see Wyllie and Huang, 1976 a) and isotherms. Vertical lines in this projection correspond to the contours in Figure 6A. The intersection of reaction (6) extends from I₆. Intersections of the surface with divariant reactions (4) and (2) need not concern us here.

the geotherm section, Figure 8A. The vapor phase is enriched in H₂O. If this is moved to deeper levels with thermal equilibrium maintained, dissociation of the carbonate will proceed, enriching the vapor in CO₂, but as long as any carbonate remains the system is constrained to remain on the divariant decarbonation surface. The last trace of carbonate reacts at point b, where the vapor reaches the composition 50% CO₂, and the system then follows path bc and melting begins at c in the presence of vapor containing 50% CO₂.

Consider the same sequence of events for a mantle containing 0.05% H₂O and 0.15% CO₂. This begins at a in Figure 8B as before, and progressive decarbonation brings the system to point b. At this point, however, with vapor phase containing 50% CO₂, there is still 0.1% CO₂ locked in crystalline carbonate, so the system continues along the reaction surface intersected in bd. The solidus temperature is reached at d before all of the carbonate has dissociated, and the silicate-carbonate assemblage thus begins to melt at d on the univariant line of Figure 6 (reaction 6); see also Figure 7A. The presence of carbonate thus buffers the vapor-phase composition at the solidus to composition d for this pressure. At different pressures, or depths, the persistence

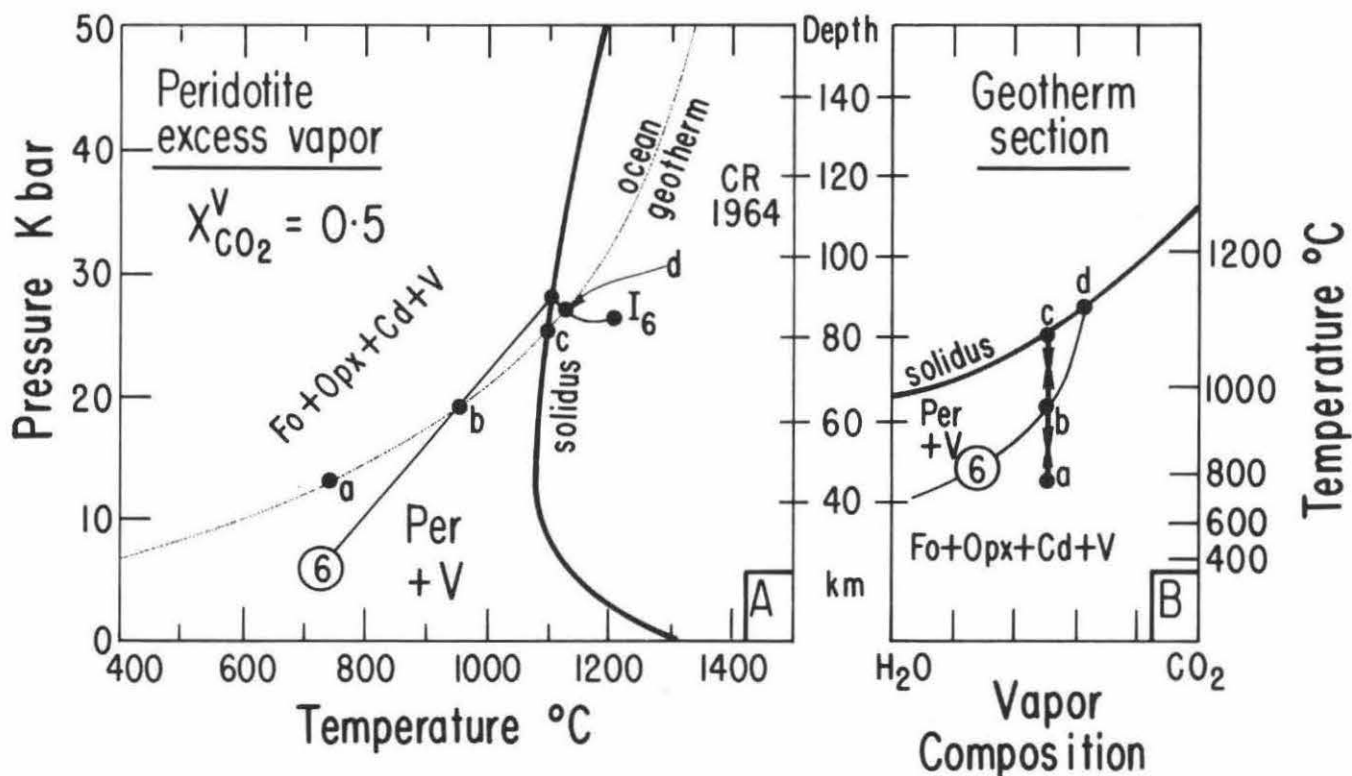


Figure 7. Peridotite-H₂O-CO₂ with excess vapor, neglecting the formation of hydrous minerals. For peridotite moving up or down the geotherm between a and c (Figure 7A) the vapor phase composition and phase fields intersected can be traced on Figure 7B. See text for discussion.

A. Isopleth with vapor of defined composition, $X_{\text{CO}_2}^{\text{V}} = 0.5$. The solidus and reaction (6) for these conditions are taken from Figure 6A—note the connection to I_6 . The geotherm for oceanic regions is that calculated by Clark and Ringwood (1964), somewhat lower in temperature than that of Ringwood (1966).

B. Geotherm section through the phase diagram for P-T- $X_{\text{CO}_2}^{\text{V}}$. This is a ruled surface parallel to the axis $X_{\text{CO}_2}^{\text{V}}$ following the geotherm of Figure 7A. The left-hand axis shows depth (pressure), and the right-hand axis shows the corresponding temperature along the geotherm. The geotherm section intersects the surfaces shown in Figure 6A. Intersections with the reactions (4) and (2) of Figure 6B are not plotted.

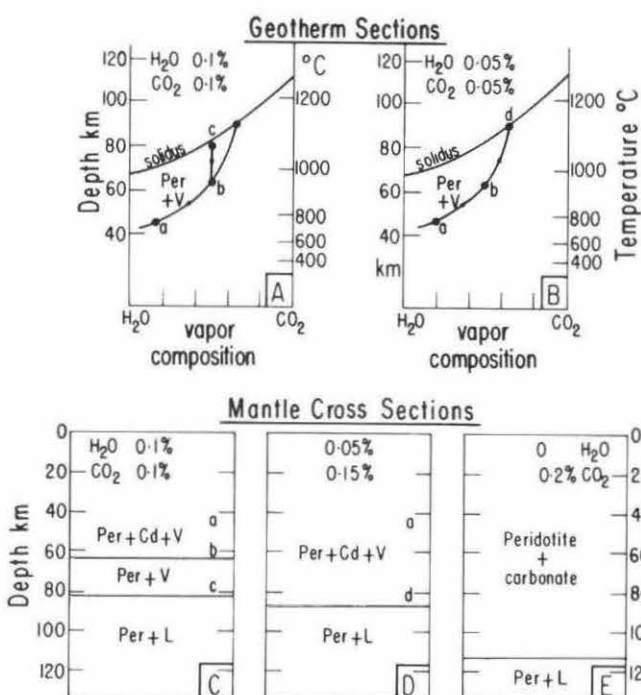


Figure 8. Geotherm sections and mantle cross-sections for peridotite-H₂O-CO₂ with small quantities of volatile components, neglecting the formation of hydrous minerals.

A and B. Geotherm sections showing phase fields intersected, corresponding to Figure 7B. See text for discussion of paths followed by peridotite-volatile assemblages on these figures and Figure 7A.

C, D, and E. Mantle cross-section with mixed volatiles H₂O-CO₂ as in figures A and B retain excess vapor until melting begins, whereas if no H₂O is present all CO₂ reacts to produce calcic dolomite in the peridotite

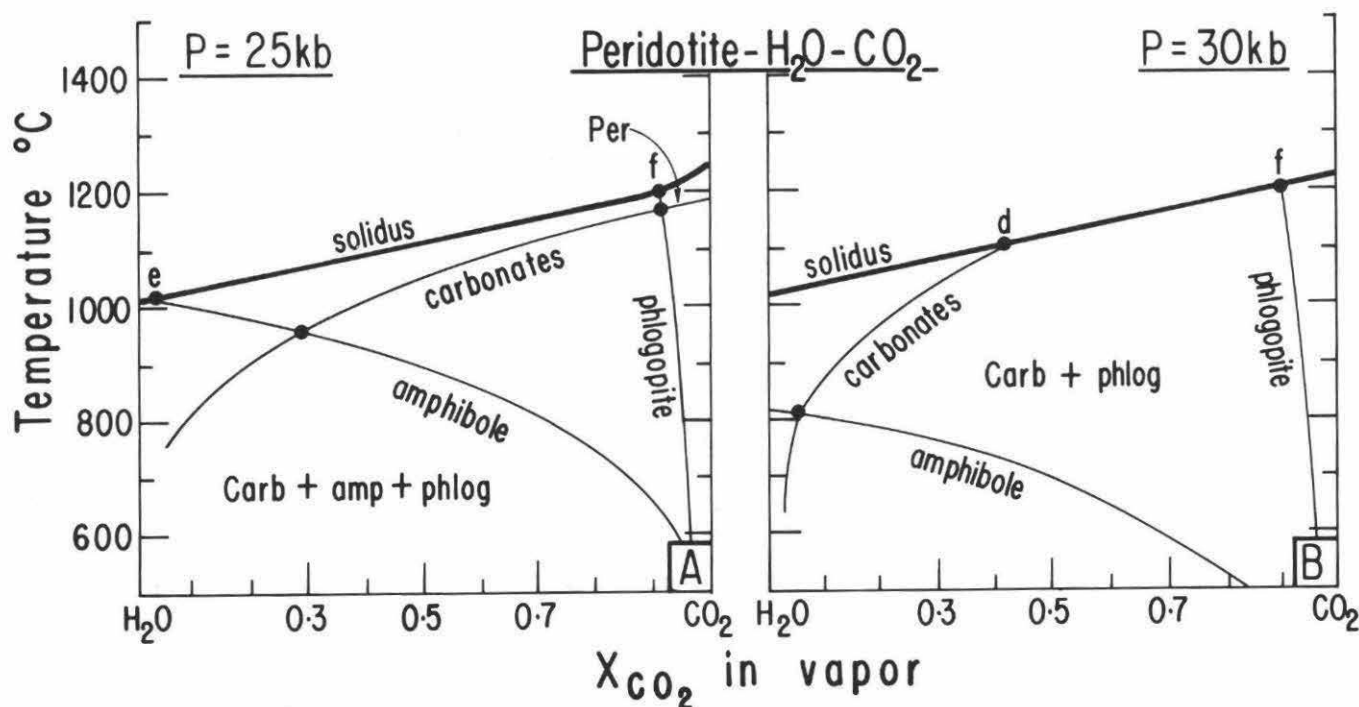


Figure 9. Schematic isobaric sections through peridotite-H₂O-CO₂ with excess vapor, corresponding to Figure 6A, with the maximum stability ranges (estimated) of the hydrous minerals, amphibole and phlogopite, added to the

curves for carbonate stability. These provide limits only. At points of intersection of the subsolidus curves isobaric invariant points will be generated, together with arrays of additional reactions.

of carbonate to the solidus would buffer vapor phase composition to values given by the univariant reaction (6) projected in Figure 6B.

The petrology of mantle cross-sections corresponding to the systems depicted in Figures 8A and B are shown in Figures 8C and D. Figure 8C shows carbonated peridotite overlying peridotite without carbonate, overlying a partially melted, vapor-absent layer. This sequence can be traced directly on Figure 7A. The vapor phase composition varies from a to b but remains constant from b to c. With a higher CO₂/H₂O ratio in the system, the carbonated peridotite persists all the way down to the partially melted layer, with vapor phase composition varying continuously from a to d (Figures 8B and 8D). For a peridotite-CO₂ mantle, Figure 8E shows that vapor-free carbonated peridotite overlies the partially melted layer (compare Figures 7A and 5).

Note that the shield geotherm would intersect the solidus at greater depths (Figure 5), and exclude the peridotite + vapor interval of Figure 8C (compare Figure 7A) except for very high values of H₂O/CO₂. According to Figure 6B, depression of the partially melted layer to deeper levels buffers the vapor phase to higher H₂O/CO₂ values. It has been established that the composition of the first liquid produced from peridotite in the presence of CO₂-H₂O vapor is strongly dependent on the vapor composition. Near-solidus liquids become more siliceous with increasing H₂O/CO₂ (Eggler, 1975b; Mysen and Boettcher, 1975b). In the presence of carbonated peridotite at pressures greater

than 25 kb, however, I anticipate that addition of H₂O will be less effective in changing near-solidus liquids away from carbonatitic compositions (Wyllie and Haas, 1965, 1966; Boettcher and Wyllie, 1969). This needs experimental verification, because it obviously has significant petrological and geophysical implications.

The stabilization of amphibole and phlogopite in the presence of H₂O-CO₂ vapors complicates the simple picture of Figures 6 to 8. Figure 9 shows two schematic isobaric sections through peridotite - H₂O-CO₂ with excess vapor. These show the divariant surface for the carbonation of peridotite, reaction (6) in Figures 5 and 6A, which gives the maximum stability range of carbonates in the system, and also the estimated maximum stability range of amphibole and phlogopite in the presence of H₂O-CO₂ vapors. These provide limits only. At points of intersection of the subsolidus curves, isobaric invariant points are generated, together with arrays of additional reactions. Examples for other systems at lower pressures can be found in Kerrick's (1974) review of metamorphic reactions with CO₂-H₂O vapors.

Compare Figure 9 with the geotherm sections of Figures 7B and 8B. The isobaric diagrams intersect the same phase boundaries and phase fields as the geotherm sections, but the geometries are different. We used Figures 7B and 8B to evaluate the influence of decarbonation reactions in buffering the vapor phase composition. Isobaric diagrams such as those in Figure 9 can be used similarly to evaluate the influence of decarbonation and dehydration reactions as buffers.

For subcontinental geotherms, the influence of amphibole is probably limited because of its limited pressure stability, as shown by comparison of Figure 9 with the geotherms in Figure 5. If compositions are suitable for the stabilization of phlogopite, however, this buffers the vapor phase composition towards CO_2 and the carbonatitic liquids. We must understand the phase relationships at mantle pressure for the system carbonate-phlogopite-vapor in the presence of peridotite in order to determine the compositions of vapors and near-solidus magmas in the mantle. I have no doubt that if the near-solidus carbonatitic liquids are generated, these will also be enriched in alkalis, and the components of phlogopite if it is present.

CARBONATE LIQUIDS IN THE SYSTEM CaO-MgO-CO_2 FROM MANTLE TO CRUSTAL PRESSURES

The preceding discussion shows that the upper part of the asthenosphere may contain interstitial carbonatite magma with only 10-15% dissolved silicates. This is a potential source for primary carbonatite magmas. Koster van Groos (1975) reached similar conclusions. It is therefore of interest to determine the phase relationships for these liquids from mantle depths to the upper crust. A first step is to examine the phase relationships in the carbonates themselves, because the phase relationships in the carbonate join exert considerable influence on the carbonate-silicate liquidus field boundary, as suggested by their proximity at high pressures in Figure 3A.

Irving and Wyllie (1973, 1975) determined subsolidus and melting relationships for the join $\text{CaCO}_3\text{-MgCO}_3$ at 30 kb, together with the fusion curves for calcite and magnesite, and the dissociation curve for magnesite below 25 kb. The results, incorporated into Figures 10A and 10B, were subsequently corrected for friction by - 3 kb when it was discovered that the glass furnace assemblies had characteristics different from talc assemblies (Huang and Wyllie, 1975, 1976).

The new experimental data were integrated with all previously published data at low pressures, reviewed in detail by Irving and Wyllie (1975), and this permitted construction of the complete P-T diagram shown in Figure 10A, together with a series of schematic isobars. The schematic isobar for 5 kb is compared with the experimentally determined 30 kb isobar in Figure 10.

Note the temperature minimum on the liquidus for carbonate solid solutions between dolomite and calcite compositions ($\text{Ccd} = \text{L}$ in Figure 10A). According to the estimates for 5 kb in Figure 10C, carbonate liquid in the crust can precipitate a calcic carbonate at a temperature near 1100° C. Unpublished experiments on this join at 10 kb, by A. P. Byrnes at the University of Chicago, suggest that the phase relationships may be more complex. The melting loop with temperature minimum passes very close to the calcite-dolomite solvus, and if these phase fields do intersect, a variety of interesting crystallization paths becomes possible.

Huang and Wyllie (1976) have extended this work by measuring the solubility of CO_2 in calcite and magnesite liquids at 30 kb, and by completing the P-T projections for CaO-CO_2 and MgO-CO_2 . Adding these data to Figure 10A permitted additional estimates of the positions of reactions with excess vapor (Wyllie and Huang, 1976a, Figure 1).

Minimum liquidus temperatures in the system CaO-MgO-CO_2 do not appear to fall below 1000°C, which is too high for intrusive carbonatites according to field evidence. The presence of dissolved iron would certainly lower that temperature. The presence of a few per cent of H_2O has a dramatic effect (Wyllie and Tuttle, 1960), and dissolved alkalis are also effective (Cooper et al, 1975). Cooper et al (1975) argued that carbonatite magmas may well have been very rich in alkalis that were since lost from the environment of the carbonatite rock. The sodium carbonate lavas of Oldoinyo Lengai in Tanzania provide unique evidence for the existence of natural liquids consisting essentially of Na_2CO_3 , CaCO_3 , and K_2CO_3 in order of decreasing abundance, together with a few per cent of halogens and sulfur, and an uncertain percentage of original H_2O (Dawson, 1966). The fact that the SiO_2 content of these lavas is less than 2% raises the question of whether or not a process of liquid immiscibility is involved.

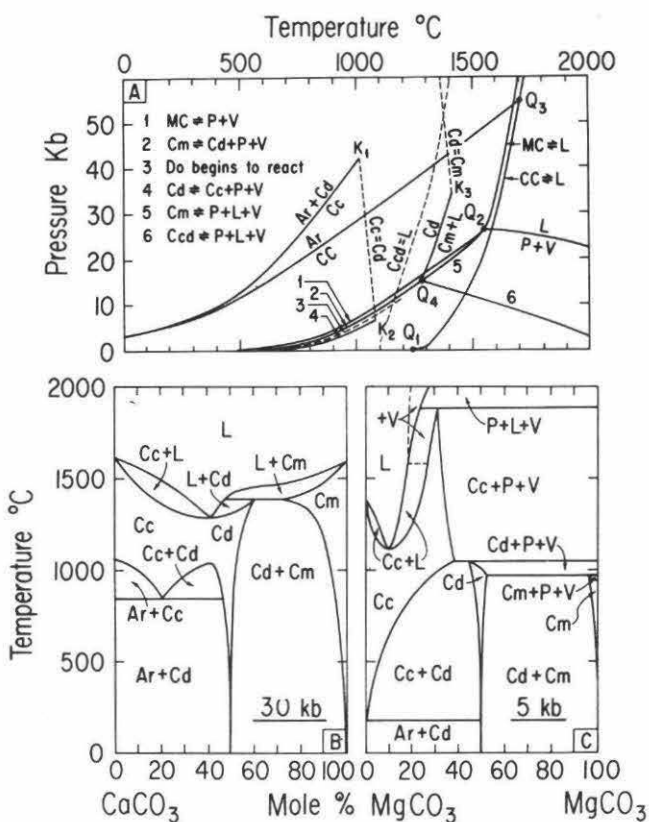


Figure 10. A. P-T projection, partly schematic, for reactions involving the join $\text{CaCO}_3\text{-MgCO}_3$, based on new experimental data and previous results combined by Irving and Wyllie (1975). B. Isobar based on 30 kb experimental data. C. Isobar based on reactions at 5 kb in Figure 10A, and other results cited by Irving and Wyllie, (1975). Abbreviations: MC = magnesite; Do = dolomite; Ar = aragonite; P = periclase; Cc, Cd, and Cm = carbonate solid solutions related to calcite, dolomite and magnesite, respectively, at lower pressures and temperatures; Ccd intermediate solid solutions; L = liquid; V = vapor.

LIQUID IMMISCIBILITY IN SILICATE-CARBONATE SYSTEMS

Koster van Groos and Wyllie (1966, 1968, 1973) examined the effect of excess alkalis on the phase relationships in silicate-carbonate systems at crustal pressures by studying phase fields intersected by composition joins from Na_2CO_3 to albite and plagioclase feldspar, with various contents of H_2O . Results for plagioclase- Na_2CO_3 - H_2O are illustrated in Figure 11. There is a large field of immiscibility between a silicate-rich liquid which is nepheline normative, and a Na-Ca-carbonate-rich liquid. Both liquids coexist with an aqueous vapor with dissolved Na_2O and CO_2 . These three phases were equated with alkaline silicate magma, carbonatite magma, and fenitizing fluid in discussions by Koster van Groos and Wyllie (1968, 1973).

Koster van Groos (1975) explored the effect of excess CO_2 under pressure on a series of rock compositions at pressures up to 10 kb, and he concluded that for most rock compositions, a separate alkali-enriched carbonate liquid could be developed through liquid immiscibility.

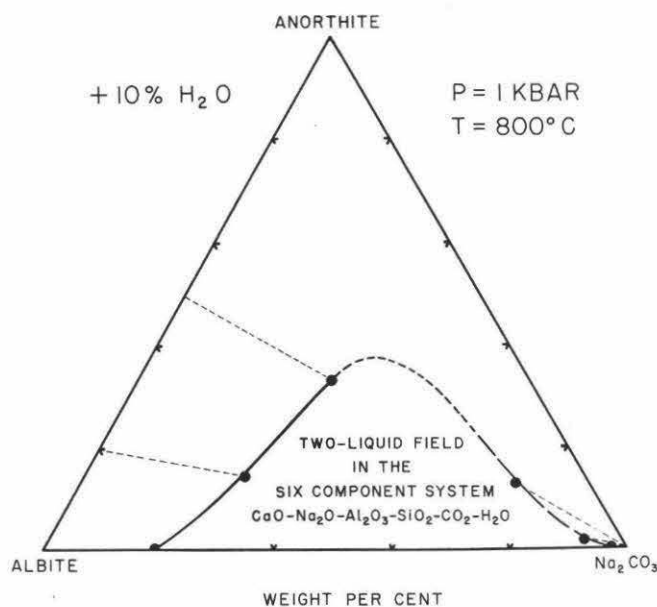


Figure 11. Liquid miscibility gap intersected by the join Ab- Na_2CO_3 with 10% H_2O at 1 kb and 800°C . The silicate liquid is enriched in nepheline components, and the carbonate liquid contains CaCO_3 components (Koster van Groos and Wyllie, 1973).

No one has yet discovered evidence for liquid immiscibility between silicates and carbonates in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$.

In their experiments with olivine-melilitite- CO_2 - H_2O , Brey and Green (1976a) reported carbonate droplets in silicate glass quenched from pressures greater than 20 kb, but concluded that they had too few experimental results to

be certain of the inference that this represented liquid immiscibility, or to propose any interpretation concerning the genesis of carbonatites.

Based on the data outlined above, I have no doubt that with addition of alkalis and other components to the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$, possibly in the form of phlogopite, a field for liquid immiscibility will be generated. Whether or not this will extend across compositional ranges of petrogenetic relevance at mantle pressures remains to be determined experimentally. But it seems very likely that it will. Liquid immiscibility may thus be involved at different stages in the history of carbonatites, from mantle derivation to crustal consolidation.

CRYSTALLIZATION AT CRUSTAL PRESSURES

The application of phase equilibrium studies to the crystallization of alkaline rocks and carbonatites has been extensively reviewed (e.g. Wyllie, 1966a, 1966b; Wyllie and Biggar, 1966, Wyllie, 1974). Koster van Groos and Wyllie (1968, 1973) discussed in particular the possible relationships among alkaline magmas, immiscible carbonatite fractions, and a third fluid phase corresponding to fenitizing solutions. Cooper et al (1975) presented experimental data for the system $\text{CaCO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ and related this to the genesis of the Oldoinyo Lengai lavas and other carbonatite problems. Watkinson and Wyllie (1971) related phase relationships in the system $\text{NaAlSi}_3\text{O}_8\text{-CaCO}_3\text{-H}_2\text{O}$ to the specific sequences of crystallization in the variegated rocks of the Oka Complex, and found remarkable similarities. The phase equilibrium data are consistent with a magmatic history for carbonatites, although there is no doubt that for many carbonatites the clarity of the evidence has been at least partly obscured by metasomatism and recrystallization caused by deformation.

The sluggish crystallization of silicate magmas often permits the preservation of a historical record of crystallization sequence. In the less viscous carbonatite magmas, however, crystal settling and consequent fractional crystallization normally disrupts the continuity of the historical record. Textures of samples quenched from phase equilibrium experiments under known conditions have been compared with textures in carbonatites, and many of these are consistent with magmatic interpretations. A characteristic feature sketched originally by Wyllie and Tuttle (1960) is the occurrence of relatively large, rounded or rhombic carbonate crystals enclosed by fine-grained dendritic matrix representing former liquid. Figure 12 illustrates some experimental charges quenched from the composition join $\text{NaAlSi}_3\text{O}_8\text{-CaCO}_3\text{-H}_2\text{O}$ (Watkinson, 1965; Watkinson and Willie, 1971). Primary calcite crystals are distinctive in Figures 12C and 12D, and euhedral melilite and spurrite are easily distinguished from quenched liquid in Figures 12A and 12B. Wyllie and Boettcher (1969) published similar photographs comparing primary calcite and aragonite enclosed in quenched liquid, and contrasting these with fine-grained subsolidus assemblages.

Gittins (1973) has described similar textures in carbonatites, and related them to the controlled processes in synthetic systems. Dendritic carbonates have since been discovered in many carbonatites (e. g. Girault, 1966; Dawson and Hawthorne, 1973).

Much of the current interest in carbonatites is concerned less with the generation of carbonatites from silicate magmas than with the distribution of minor elements and their host minerals within the magmatic complexes. Abundant apatite is a characteristic feature of nearly all carbonatites, and it constitutes a significant source of phosphates. It typically forms ovoid grains or, less commonly, radial or parallel clusters of slender prisms (Heinrich, 1966, p. 176-177). Both of these textures have been reproduced in laboratory experiments, as illustrated in Figure 13.

Biggar (1969) completed a series of experimental studies on carbonate-apatite systems (summarized in Wyllie and

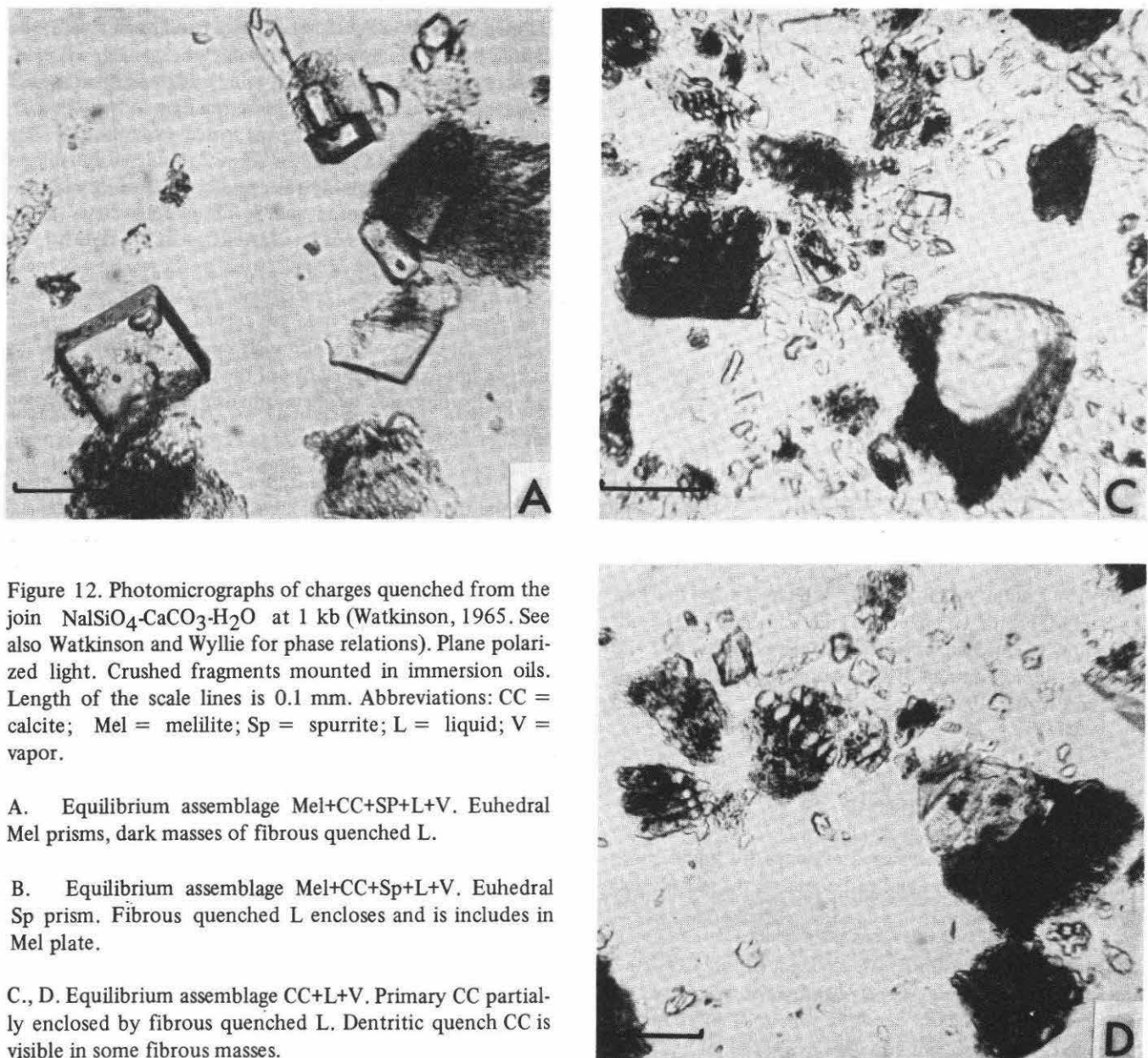


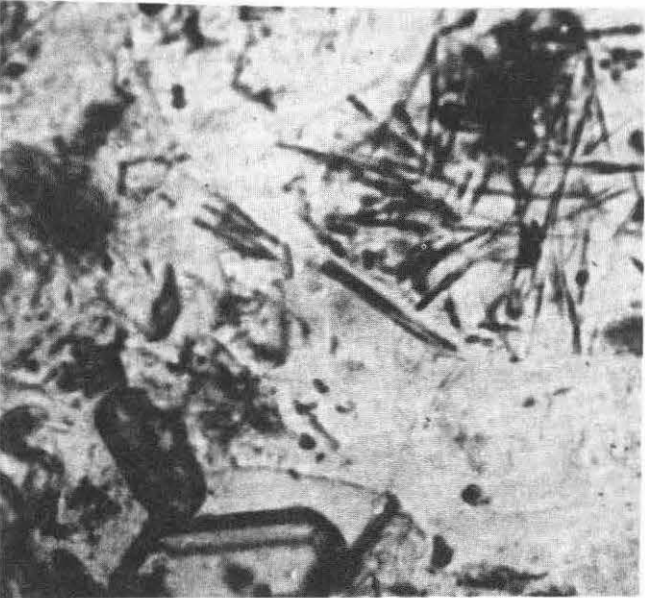
Figure 12. Photomicrographs of charges quenched from the join $\text{NaSiO}_4\text{-CaCO}_3\text{-H}_2\text{O}$ at 1 kb (Watkinson, 1965. See also Watkinson and Wyllie for phase relations). Plane polarized light. Crushed fragments mounted in immersion oils. Length of the scale lines is 0.1 mm. Abbreviations: CC = calcite; Mel = melilite; Sp = spurrite; L = liquid; V = vapor.

A. Equilibrium assemblage Mel+CC+SP+L+V. Euhedral Mel prisms, dark masses of fibrous quenched L.

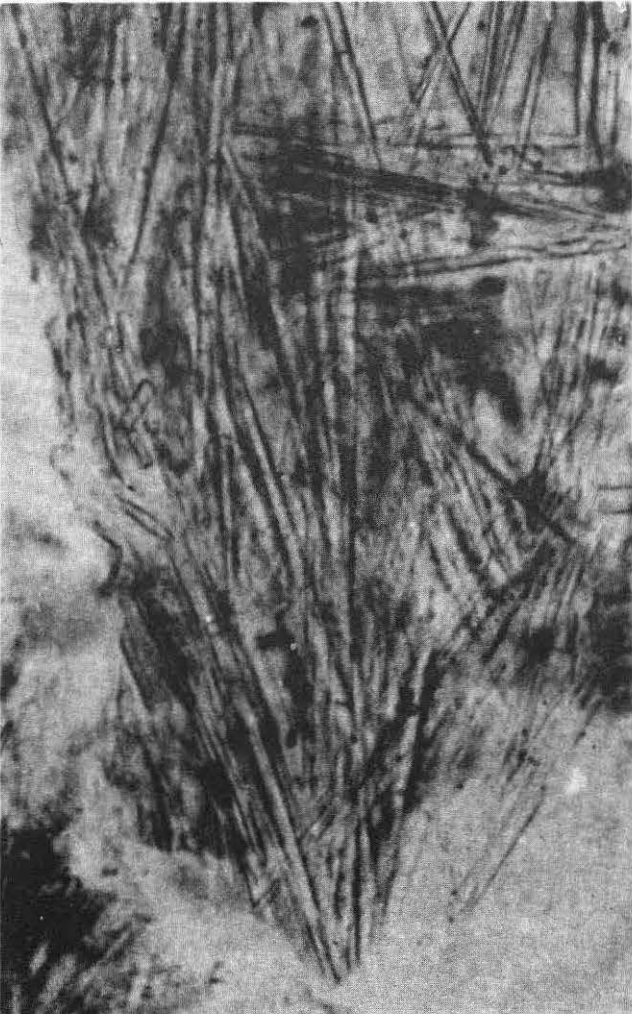
B. Equilibrium assemblage Mel+CC+Sp+L+V. Euhedral Sp prism. Fibrous quenched L encloses and is includes in Mel plate.

C., D. Equilibrium assemblage CC+L+V. Primary CC partially enclosed by fibrous quenched L. Dendritic quench CC is visible in some fibrous masses.

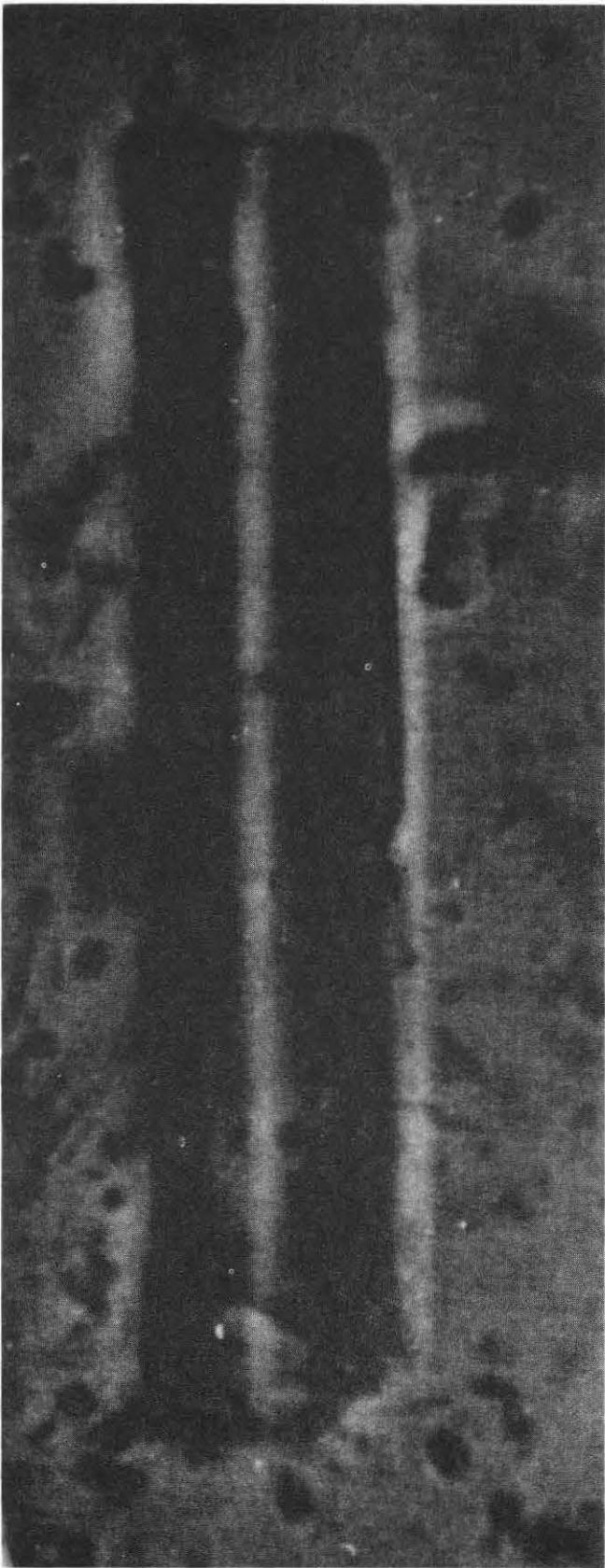
Figure 13. Synthetic apatite crystals in crushed fragments from charges quenched from high pressures and temperatures in apatite- CaCO_3 - Ca(OH)_2 - CaF_2 systems (Biggar, 1969; photographs from Wyllie et al, 1962). Fragments in immersion oils, with plane polarized light. Most examples are apatites precipitated from the liquid during rapid cooling.



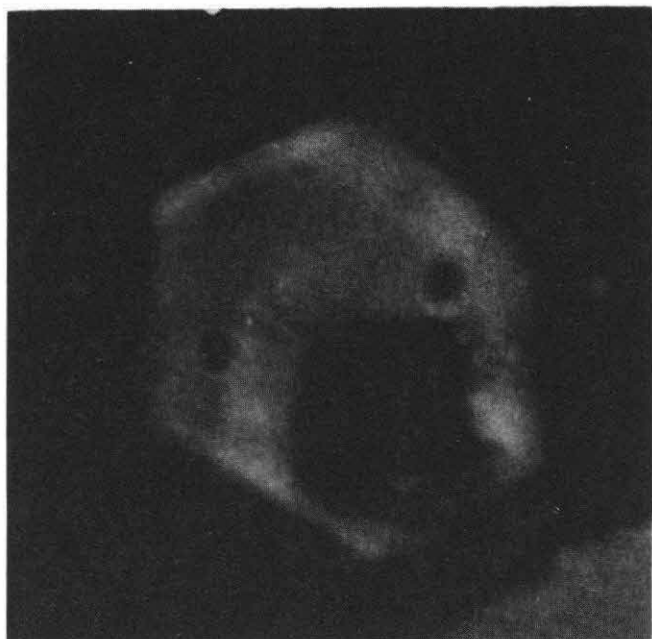
A. Primary apatite crystals, bottom left. Acicular apatite crystals in portlandite matrix, top right. Scale: X 75.



B. Aggregate of sub-parallel quench apatite needles. Scale: X 50.



C. Skeletal apatite needle with central cavity containing portlandite. Scale: X 500.



D. Cross-section of an apatite needle with a cavity containing fluorspar matrix. Scale: X 1000.



E. Cross-section of an elaborate sheaf of apatite needles, approximately hexagonal in outline. Scale: X 800.

Biggar, 1966; Willie, 1966b), and concluded that a carbonatite magma containing a small percentage of P_2O_5 would precipitate calcite and apatite together through a wide temperature interval. Apatite crystals coexisting in equilibrium with liquid or vapor in the experiments were small and equant, as illustrated in Figure 13A, whereas those precipitated from a melt during rapid quenching formed acicular prisms exhibiting a variety of parallel and skeletal growths, as shown in Figures 13A-E. The extreme fluidity of these liquids is demonstrated by the fact that even the long apatite needles precipitated from the liquid during a quench tended

to settle towards the bottom of the capsule containing the sample. There is little difficulty in accounting for the observed flow banding and segregation of apatite on the basis of a magmatic carbonatite intrusion.

The observation of cavities in apatites from the experimental studies led me to suggest (Wyllie, 1966b, p. 327) that: "Detailed examination of apatites in carbonatites might be worthwhile. For example, material enclosed by dendritic or skeletal apatites could provide information about the composition of the magma from which the apatites crystallized. This might be one of the most promising places to seek portlandite and other hydrated phases which are readily altered to carbonates by migrating CO_2 ".

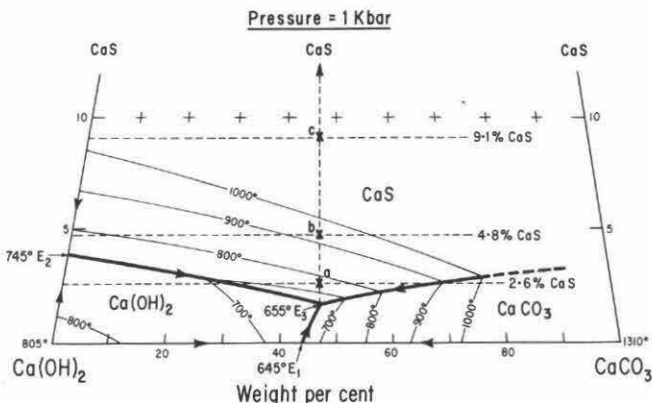


Figure 14. Liquidus surface for the system $CaCO_3$ - CaS - $Ca(OH)_2$ at 1 kb. For $CaCO_3$ - $Ca(OH)_2$ see Wyllie and Tuttle (1960) and Wyllie and Raynor (1965). Dashed lines represent experiments by G. R. Helz and Wyllie (1964 experiments, manuscript in preparation).

Rankin and Le Bas (1974) have recently published some remarkable photographs of tubular cavities in apatites from some East African carbonatites and ijolites. The inclusions in apatites from ijolite include material originally present as silicate melt, carbonate-rich melt, as aqueous fluid phase (now nahcolite-bearing), and CO_2 -vapor. Some inclusions demonstrate the simultaneous coexistence of immiscible silicate-rich and carbonate-rich melts in the ijolite magma. These observations are consistent with the experimental liquid immiscibility illustrated in Figure 11, and with the precipitation of nahcolite from the vapor phase in the experiments of Watkinson and Wyllie (1971) on the join $NaAlSiO_4$ - $CaCO_3$ - H_2O .

Pyrite is the only common sulfide in carbonatites, occurring usually as disseminated euhedral crystals (Heinrich, 1966, p. 181). At Palabora, however, chalcopyrite is sufficiently abundant to form copper ore bodies. We, therefore, took a first step towards investigation of the behavior of sulfides in carbonate systems by determining the liquidus relationships in the systems $CaCO_3$ - CaS - $Ca(OH)_2$, with results shown in Figure 14 (Helz and Wyllie, 1964, unpublished).

The phase relationships are similar to those for the carbonate-apatite systems. Only a small percentage of CaS dissolves in the carbonate-rich liquid before a field boundary is reached. Therefore, with precipitation of calcite from a carbonatite magma, the liquid should reach the field boundary at a reasonably high temperature, permitting calcite and a sulfide to coprecipitate through a wide temperature interval.

CONCLUSIONS AND GEOLOGICAL APPLICATIONS

(1) For a lithosphere peridotite with CO₂, the CO₂ would be stored as carbonate, with the possible exception of oceanic environments with rather high geotherms, where free CO₂ could exist through limited depth intervals.

(2) For a lithosphere peridotite with CO₂ and H₂O, carbonated peridotite coexists with mixed CO₂-H₂O vapors whose composition is buffered by the carbonation reaction.

(3) For a lithosphere peridotite with CO₂ and H₂O, and composition suitable for the stabilization of phlogopite, the vapor phase composition is buffered by reactions involving carbonate and phlogopite.

(4) For a mantle peridotite with CO₂, and also for CO₂ with some H₂O (limits unknown), the liquid at the top of the asthenosphere is carbonatitic, with Ca/Mg ratio greater than 1. The liquid is probably enriched in alkali carbonates, as well.

(5) Under static conditions, the interstitial liquid in the asthenosphere would change in composition from carbonatitic in the upper levels towards kimberlitic at deeper levels.

(6) Carbonatitic liquids are very fluid, and if they exist in the asthenosphere they would probably migrate upwards. Local intrusions into the overlying lithosphere, or local cooling of the asthenosphere, could produce a layer near the lithosphere-asthenosphere boundary that is enriched in crystalline carbonates, which could include aragonite (compare Figures 5, 7A, and 10).

(7) The proposal of Boyd and Nixon (1973) that kimberlite "magmas" may be mixtures of silicate liquids and carbonatitic liquids from the asthenosphere is compatible with the above conclusions. They are also consistent with the suggestion of Franz and Wyllie (1967) that carbonatite magmas could be the fluids involved in the fluidization emplacement of some kimberlites.

(8) For a mantle peridotite with high H₂O/CO₂, the interstitial liquid in the upper asthenosphere may be a silicate melt rather than carbonatitic, but it is very likely that an immiscible alkali-rich carbonatitic liquid will separate from the silicate liquid, in amounts controlled by the CO₂/H₂O ratios and alkali content.

(9) Primary carbonatite magmas may be derived from the upper asthenosphere.

(10) Eruption of CO₂-undersaturated magmas from the asthenosphere layer may become explosive at depths near 80 km where CO₂ must be evolved as the liquid crosses the boundary (I₁Q₆)-S₁ in Figure 5.

(11) Carbonated alkali peridotite magmas (broadly kimberlitic, or nepheline-melilititic) may be derived as parental magmas from the asthenosphere, producing derivative magmas in the crust corresponding to alkaline complexes and carbonatites. The process in the crust may include fractional crystallization and liquid immiscibility. Either process is capable of generating fluids that fenitize the country rocks.

(12) Accessory minerals such as apatite and pyrite have limited solubility in carbonatite magmas, and therefore are likely to be precipitated alongside carbonate through a wide temperature interval.

ACKNOWLEDGMENTS

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BIBLIOGRAPHY

- Ahrens, L. H., Dawson, J. B., Duncan, A. R., and Erlank, A. J., 1975. (Editors) *Physics and Chemistry of the Earth. Vol. 9*, Oxford, Pergamon Press.
- Biggar, G. M., 1969. Phase relationships in the join Ca(OH)₂-CaCO₃-Ca₃(PO₄)₂-H₂O at 1000 bars. *Miner. Mag.*, 37, 75-82.
- Boettcher, A. L., and Wyllie, P. J., 1969. The system CaO-SiO₂-CO₂-H₂O: III. A second critical end-point on the melting curve at 32.5 kbars and 515° C. *Geochim. Acta*, 33, 611-632.
- Bowen, N. L., 1940. Progressive metamorphism of siliceous limestone and dolomite. *Jour. Geol.*, 48, 225-274.
- Boyd, F. R., and Nixon, P. H., 1973. Origin of the ilmenite-silicate nodules in kimberlites from Lesotho and South Africa. In Nixon, P. H., editor, *Lesotho Kimberlites*. Maseru, Lesotho National Development Corporation, 254-268.
- Brey, G. P., and Green, D. H., 1975. The role of CO₂ in the genesis of olivine melilitite. *Contrib. Mineral. Petrol.*, 49, 93-103.
- Brey, G. P., and Green, D. H., 1976a. Solubility of CO₂ in olivine melilitite at high pressures and role of CO₂ in the earth's upper mantle. *Contr. Mineral. Petrol.*, 55, 217-230.
- Brey, G. P., and Green, D. H., 1976b. Reply to Eggler and Mysen. *Contr. Mineral. Petrol.*, 55, 237-239.
- Clark, S. P., and Ringwood, A. E., 1964. Density distribution of the mantle. *Review Geophysics*, 2, 35-88.
- Cooper, A. F., Gittins, J., and Tuttle, O. F., 1975. The system Na₂CO₃-K₂CO₃-CaCO₃ at 1 kilobar and its significance in carbonatite petrogenesis. *Amer. Jour.*

- Sci., 275, 534-560.
 Mine, Transvaal. Jour. Geol., 33, 659-684.
- Daly, R.A., 1925. Carbonate dikes of the Premier Diamond Mine, Transvaal. Jour. Geol., 33, 659-684.
- Dawson, J.B., 1966. Oldoinyo Lengai—an active volcano with sodium carbonatite lava flows. In Tuttle, O. F., and Gittins, J., editors, "Carbonatites". Interscience Publishers, New York, 155-168, 591 p.
- Dawson, J. B., and Hawthorne, J. B., 1973. Magmatic sedimentation and carbonatitic differentiation in kimberlite sills at Benfontein, South Africa. Quart. Jour. Geol. Soc. Lond., 129, 61-85.
- Eggler, D. H., 1974. Effect of CO_2 on the melting of peridotite. Carnegie Inst. Washington Year Book, 73, 215-224.
- Eggler, D. H., 1975a. Carbonatite generation by a reaction relation in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$ at 30 kbar pressure (abs). EOS (Am. Geophys. Union Trans.), 56, 470.
- Eggler, D. H., 1975b. Peridotite-carbonate relations in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$. Carnegie Inst. Washington Year Book, 74, 468-474.
- Eggler, D. H., 1976. Does CO_2 cause partial melting in the low-velocity layer of the mantle? Geology, 4, 69-72.
- Eggler, D. H., and Mysen, B. O., 1976. The role of CO_2 in the genesis of olivine melilitite: discussion. Contr. Mineral. Petrol., 55, 231-236.
- Eggler, D. H., Holloway, J. R., and Mysen, B. O., 1976. High CO_2 solubilities in mantle magmas: comment. Geology, 4, 198-199.
- Franz, G. W., and Wyllie, P. J., 1967. Experimental studies in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$. In Wyllie, P. J., editor, Ultramafic and Related Rocks. Wiley & Sons, Inc., New York, 323-326.
- Girault, J., 1966. Genese et geochimie de l'apatite et de la calcite dans les roches liees au complexe carbonatique et hyperalcalin d'Oka (Canada). Soc. Française Mineral. Bull., 84, 496-513.
- Gittins, J., 1973. The significance of some porphyritic textures in carbonatites. Can. Mineral. 12, 226-228.
- Heinrich, E. W., 1966. The Geology of Carbonatites. Rand McNally and Co., Chicago, 607 p.
- Huang, W. L., and Wyllie, P. J., 1974. Eutectic between wolastonite II and calcite contrasted with thermal barrier in $\text{MgO-SiO}_2\text{-CO}_2$ at 30 kilobars, with applications to kimberlite-carbonatite petrogenesis. Earth & Planet. Sci. Letters, 24, 305-310.
- Huang, W. L., and Wyllie, P. J., 1975. Melting reactions in the system $\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-SiO}_2$ to 35 kilobars, dry and with excess water. Jour. Geol., 83, 737-748.
- Huang, W. L., and Wyllie, P. J., 1976. Melting relationships in the systems CaO-CO_2 and MgO-CO_2 to 33 kilobars. Geochim. Cosmochim. Acta, 40, 129-132.
- Irving, A. J., and Wyllie, P. J., 1973. Melting relationships in CaO-CO_2 and MgO-CO_2 to 36 kilobars, with comments on CO_2 in the mantle. Earth and Planet. Sci. Lett., 20, 220-225.
- Irving, A. J., and Wyllie, P. J., 1975. Subsolvus and melting relationships for calcite, magnesite, and the join $\text{CaCO}_3\text{-MgCO}_3$ to 36 kilobars. Geochim. Cosmochim. Acta, 39, 35-53.
- Kerrick, D. M., 1974. Review of metamorphic mixed volatile ($\text{H}_2\text{O-CO}_2$) equilibria. Amer. Miner., 59, 729-762.
- King, B. C., 1965. Petrogenesis of the alkaline igneous rock suites of the volcanic and intrusive centres of eastern Uganda. Jour. Petrology, 6, 67-100.
- Koster van Groos, A. F., 1975. The effect of high CO_2 pressures on alkalic rock and its bearing on the formation of alkalic ultrabasic rocks and the associated carbonatites. Amer. Jour. Sci., 275, 163-185.
- Koster van Groos, A. F., and Wyllie, P. J., 1966. Liquid immiscibility in the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$ at pressures up to 1 kilobar. Amer. Jour. Sci., 264, 234-255.
- Koster van Groos, A. F., and Wyllie, P. J., 1968. Liquid immiscibility in the join $\text{NaAlSi}_3\text{O}_8\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ and its bearing on the genesis of carbonatites. Amer. Jour. Sci., 266, 932-967.
- Koster van Groos, A. F., and Wyllie, P. J., 1973. Liquid immiscibility in the join $\text{NaAlSi}_3\text{O}_8\text{-CaAlSi}_2\text{O}_8\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$. Amer. Jour. Sci., 273, 465-487.
- Maale, S., and Wyllie, P. J., 1975. Water content of a granite magma deduced from the sequence of crystallization determined experimentally with water-undersaturated conditions. Contr. Mineral. Petrol., 52, 175-191.
- Merrill, R. B., and Wyllie, P. J., 1973. Absorption of iron by platinum capsules in high pressure rock melting experiments. Amer. Min., 58, 16-20.
- Merrill, R. B., and Wyllie, P. J., 1975. Kaersutite and kaersutite eclogite from Kakanui, New Zealand Water-excess and water-deficient melting at 30 kilobars. Geol. Soc. Amer. Bull., 86, 555-570.
- Millhollen, G.L., and Wyllie, P.J., 1974. Melting relations of brown-hornblende mylonite from St. Paul's Rocks under water-saturated and water-undersaturated conditions to 30 kilobars. Jour. Geol., 82, 589-606.
- Millhollen, G. L., Irving, A. J., and Wyllie, P. J., 1974. Melting interval of peridotite with 5.7 per cent water to 30 kilobars. Jour. Geol. 82, 575-587.
- Mysen, B. O., and Boettcher, A. L., 1975a. Melting of a hydrous mantle: I. Phase relations of natural peridotite at high pressures and temperatures with controlled activities of water, carbon dioxide, and hydrogen. Jour. Petrology, 16, 520-548.
- Mysen, B. O., and Boettcher, A. L., 1975b. Melting of a hydrous mantle: II. Geochemistry of crystals and liquids formed by anatexis of mantle peridotite at high pressures and high temperatures as a function of controlled activities of water, hydrogen, and carbon dioxide. Jour. Petrology, 16, 549-593.
- Mysen, B. O., Eggler, D. H., Seitz, M. G., and Holloway, J. R., 1976. Carbon dioxide in silicate melts and crystals. I. Solubility measurements. Amer. Jour. Sci., 276, 455-479.
- Nehru, C.E., and Wyllie, P.J., 1975. Compositions of glasses from St. Paul's peridotite partially melted at 20 kilobars. Jour. Geol., 83, 455-471.
- Newton, R. C., and Sharp, W. E., 1975. Stability of forsterite + CO_2 and its bearing on the role of CO_2 in the

- mantle. *Earth and Planet. Sci. Letters*, 26, 239-244.
- Rankin, A. H., and Le Bas, M. J., 1974. Liquid immiscibility between silicate and carbonate melts in naturally occurring ijolite magma. *Nature*, 250, 206-209.
- Ringwood, A. E., 1966. Mineralogy of the mantle. In Hurley, P. M., editor, *Advances in Earth Sciences. M. I. T. Press, Cambridge, Massachusetts*, 357-399.
- Turner, F. J., 1968. *Metamorphic Petrology*. McGraw-Hill, New York, 403 p.
- Watkinson, D. H., 1965. Melting relationships in parts of the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$ with applications to carbonate and alkalic rocks. Ph. D. dissertation, The Pennsylvania State University.
- Watkinson, D. H., and Wyllie, P. J., 1971. Experimental study of the join $\text{NaAlSi}_3\text{O}_8-\text{CaCO}_3-\text{H}_2\text{O}$ and the genesis of alkalic rock-carbonatite complexes. *Jour. of petrology*, 12, 357-378.
- Watson, K. D., 1955. Kimberlite at Bachelor Lake, Quebec. *Amer. Mineral.*, 40, 565-579.
- Wimmenauer, W., 1966. The eruptive rocks and carbonatites of the Kaiserstuhl, Germany. In Tuttle, O. F., and Gittins, J., editors, *Carbonatites*. Interscience Publishers, New York, 183-204, 591 p.
- Wyllie, P. J., 1966a. Experimental data bearing on the petrogenetic links between kimberlites and carbonatites. *Papers and Proceedings of the 4th General Meeting, International Mineralogical Association, I.M.A. Volume, Mineral. Soc. India*, 67-82.
- Wyllie, P. J., 1966b. Experimental studies of carbonatite problems: the origin and differentiation of carbonatite magmas. In Tuttle, O. F., and Gittins, J., editors, *The Carbonatites*. John Wiley & Sons, Inc., 311-352.
- Wyllie, P. J., 1974. Limestone assimilation. In Sørensen, H., editor, *Alkaline Rocks*. Wiley & Sons, Chapter VI. 3, 459-474, 622 p.
- Wyllie, P. J., 1976. Experimental studies on the influence of CO_2 and H_2O in the upper mantle. *Proceedings of U. S. - Japan conference on "High Pressure Research Applications in Geophysics"*, Hawaii.
- Wyllie, P. J., and Biggar, G. M., 1966. Fractional crystallization in the "carbonatite systems" $\text{CaO}-\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ and $\text{CaO}-\text{CaF}_2-\text{P}_2\text{O}_5-\text{CO}_2-\text{H}_2\text{O}$. *Papers and Proceedings of the 4th General Meeting, International Mineralogical Association, I.M.A. Volume, Mineral. Soc. India*, 92-105.
- Wyllie, P. J., and Boettcher, A. L., 1969. Liquidus phase relationships in the system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ to 40 kilobars pressure with petrological applications. *Amer. Jour. Sci.*, J. Frank Schairer Volume, 267A, 489-508.
- Wyllie, P. J., and Haas, J. L., 1965. The system $\text{CaO}-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$: I. Melting relationships with excess vapor at 1 kilobar pressure. *Geochim. Cosmochim. Acta*, 29, 871-892.
- Wyllie, P. J., and Haas, J. L., 1966. The system $\text{CaO}-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$: II. The petrogenetic model. *Geochim. Cosmochim. Acta*, 30, 525-544.
- Wyllie, P. J., and Huang, W. L., 1975. Peridotite, kimberlite, and carbonatite explained in the system $\text{CaO}-\text{MgO}-\text{SiO}_2-\text{CO}_2$. *Geology*, 3, 621-624.
- Wyllie, P. J., and Huang, W. L., 1976a. Carbonation and melting reactions in the system $\text{CaO}-\text{MgO}-\text{SiO}_2-\text{CO}_2$ at mantle pressures with geophysical and petrological applications. *Contrib. Mineral. Petrol.*, 54, 79-107.
- Wyllie, P. J., and Huang, W. L., 1976b. High CO_2 solubilities in mantle magmas. *Geology*, 4, 21-24.
- Wyllie, P. J., and Huang, W. L., 1976c. High CO_2 solubilities in mantle magmas: reply. *Geology*, 4, 199-200.
- Wyllie, P. J., and Raynor, E. J., 1965. D.T.A. and quenching methods in the system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$. *Amer. Miner.*, 50, 2077-2082.
- Wyllie, P. J., and Tuttle, O. F., 1959a. Melting of calcite in the presence of water. *Amer. Miner.*, 44, 453-459.
- Wyllie, P. J., and Tuttle, O. F., 1959b. Effect of carbon dioxide on the melting of granite and feldspars. *Amer. Jour. Sci.*, 257, 648-655.
- Wyllie, P. J., and Tuttle, O. F., 1960. The system $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ and the origin of carbonatites. *Jour. Petrology*, 1, 1-46.
- Wyllie, P. J., Cox, K. G., and Biggar, G. M., 1962. The habit of apatite in synthetic and igneous systems. *Jour. Petrology*, 3, 238-243.

DISCUSSION

Question from — DARCY P. SVISERO - (Brazil)

Which are the evidences for carbonatites magma in the low velocity zone?

Answer — There is no direct evidence at all. Geophysicists tell us that the best interpretation for the seismic velocities is that the low velocity zone contains a trace of melt. Experimental studies tell us that if there is a trace of H_2O present, then there must be some melt at the appropriate depth. The recent work with CO_2 tell us that if there is a trace of CO_2 in the mantle, melting begins also at the appropriate depth. Pure H_2O gives a SiO_2 -undersaturated silicate magma. Pure CO_2 gives a carbonatitic magma with only, 10 – 15% dissolved silicate components. Therefore, if the mantle has CO_2 , or $\text{CO}_2 + \text{H}_2\text{O}$ with CO_2 dominant, then a trace of interstitial carbonate melt must develop in the mantle, at a depth that corresponds closely to measured depths to the top of the low-velocity zone.

Question from — AIDA ESPINOLA — (Brazil)

Is there a special reason for not having taken into consideration the water content in the present diagram and interpretation? Wouldn't a water content affect the ions activity significantly and possibly affect the distribution coefficient between the carbonate and silicate phases? May be a much more significant role in the case of ions of multiple stages of oxidation?

Answer — In all of the experiments related to Crustal processes, H_2O has been a component of the systems studied.

For studies at mantle processes, much work with H_2O has been completed. The recent work has concentrated on CO_2 without water, so as to unravel the specific role of

CO₂. In the written version of this paper I have included diagrams for peridotite - CO₂-H₂O.

You are quite correct. Water is a very influential component, and it certainly changes the phase-diagram with res-

pect to the position of the silicate-carbonate field boundary. The only reason for not having taken water into account is lack of time. We are currently investigating the effect of phlogopite as a component in the silicate-carbonate melting relationships. Perhaps next time we meet I can discuss the effect of water-and alkalis and alumina.